

PATENT

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STATEMENT BY TRANSLATOR UNDER 37 C.F.R. § 1.55

Assistant Commissioner for Patents
Alexandria, VA 22314

Commissioner:

I hereby confirm that the English translation enclosed herewith is an accurate translation of the Japan Patent Application No. 2003-039613 which was filed on February 18, 2003.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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[AMOUNT] 21,000

[LIST OF ATTACHED DOCUMENTS]

[NAME] Specification 1

[NAME] Abstract 1

[Name of Document] Specification

[Title of the invention] GLASS COMPOSITION

[Claims]

[Claim 1] A glass composition of a multicomponent oxide glass manufactured by melting glass raw materials, containing:

10 ppm or more of at least one type of a polyvalent element, minimum valence cations of the polyvalent element in a ratio of a minimum valence cation content to a total polyvalent element content of 5 to 98% in mass ratio; and

0.01 to 2 $\mu\text{l/g}$ (0°C, 1 atm) of helium.

[Claim 2] A glass composition according to claim 1, further containing at least one of 1 ppm or more in mass ratio of F, Cl, and SO₃; or 10 ppm or more in mass ratio of OH.

[Claim 3] A glass composition according to claim 1 or 2, wherein the ratio of the minimum valence cation content to the total polyvalent element content is higher by 0.1 to 40% in mass ratio compared to the ratio of a glass composition manufactured by melting in an oxygen-containing atmosphere.

[Claim 4] A glass composition according to any one of claims 1 to 3, wherein 1 ppm or more of the polyvalent element is existent in the glass composition in the state of cations having one or more valence.

[Claim 5] A glass composition according to any one of claims 1 to 4, wherein the polyvalent element is any one of V, Cr, Mn,

Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Y, Zr, Mo, Rh, Ag, Cd, Sn, Sb, Te, Ti, Pt, Au, and Bi.

[Claim 6] A glass composition according to any one of claims 1 to 5, wherein a ratio of a divalent cation content of Sn to a total Sn content is 20 to 50% in mass ratio.

[Claim 7] A glass composition according to any one of claims 1 to 6, wherein a ratio of a trivalent cation content of Sb to a total Sb content is 70% or more in mass ratio.

[Claim 8] A glass composition according to any one of claims 1 to 7, wherein a ratio of a trivalent cation content of As to a total As content is 60% or more in mass ratio.

[Claim 9] A glass composition according to any one of claims 1 to 8, wherein a ratio of a divalent cation content of Fe to a total Fe content is 30% or more in mass ratio.

[Detailed explanation of the invention]

[0001]

[Field of the Invention]

The present invention relates to a glass composition, especially a glass composition wherein bubble defects therein are reduced by means of reducing a dissolved gas in glass.

[0002]

[Prior art]

A glass composition is generally used in various applications as glass products by heating various salts, oxides, or the like

such as inorganic minerals as raw materials to high temperatures for forming molten glass, deaerating gas generated through a reaction for fining the molten glass, subsequently homogenizing the molten glass through an operation such as stirring, and then molding the molten glass into a required shape through a specific molding method. An initial problem in manufacturing such a glass composition involves how complete deaeration of minute air bubbles existing in the molten glass can be carried out during melting to provide homogeneous glass, in other words, how reliable fining can be conducted.

[0003]

Accordingly, various methods have been studied thus far for overcoming the problem of fining. A method, which is most commonly used, involves adjusting and mixing in advance a trace additive, so-called a fining, into raw materials to be melted and deaerated fine bubbles in the molten glass through a desired chemical reaction at high temperatures. Further, as another method which may be adopted, there is given a method of maintaining the molten glass in a reduced-pressure or vacuum environment by adjusting an external pressure of the environment itself in which the molten glass resides.

[0004]

Various additives have been used as fining for the former method, and appropriate fining have been selected in response to diversification of glass materials involved in expansion of applications of the glass products. Further, various studies have

been conducted on the latter method as well to develop many inventions regarding this technique.

[0005]

Regarding the former method, proposed in Patent document 1 is a method of directly introducing a clearer into an air bubble layer of a glass melting furnace instead of mixing a clearer into raw materials in advance. Further, proposed in Patent document 2 is an antimony clearer replacing an existing clearer such as an arsenic (As) clearer used thus far.

[0006]

On the other hand, regarding the latter method, proposed in Patent document 3 is a manufacture method for glass including a sub-atmospheric pressure step in which the molten glass produced in a melting step is depressurized for sub-atmosphere. However, this method becomes feasible with use of a large-scale pressure-reducing vacuum system, posing a problem of a high equipment cost. In view of the above, Patent document 4 discloses a furnace material, used for channels of the pressure-reducing vacuum system, formed of a prescribed electric fused refractory instead of a precious metal such as platinum. Further, Patent document 5 discloses a devised structure of a bubble collector which deaerates air dissolved in the glass.

[0007]

Further, dating back 20 years or more, as disclosed in Patent

document 6, a method of using helium gas as a assist means of fining glass was proposed, in which borosilicate glass is used as an object of the fining.

[0008]

[Patent document 1]

JP 6-293523 A (page 2)

[Patent document 2]

JP 11-35338 A (pages 2-5, figure 1)

[Patent document 3]

JP 2000-128549 A (pages 2-8, figures 1-2)

[Patent document 4]

JP 2000-247647 A (pages 2-8, figures 1-2)

[Patent document 5]

JP 2001-220149 A (pages 2-3, figures 1-2)

[Patent document 6]

US 3,622,296

[0009]

[Problem to be solved by the invention]

Of the fining methods of molten glass described above, the method using a fining has a problem in that stable manufacture of glass may not be necessarily sustained even when an optimal fining of a specific grade is selected at the beginning of the manufacture. This is because a grade of the glass manufactured may be at an unsatisfactory level regarding bubble defects from influences of

unavoidable causes such as variation of manufacture conditions. Further, trace components are used as additives, and thus, the fining must be capable of uniformly exhibiting its effect in the molten glass by preventing segregation or the like during mixing of the raw materials.

[0010]

Further, the latter method using a pressure-reducing device also requires responses to basic problems arising from theoretical restrictions of the method, even if the high equipment cost can be handled to some extent. That is, evaporation (also referred to as vaporization) of glass components from the molten glass is hardly prevented when using the pressure-reducing device. Therefore, this method may have to be applied to limited glass applications rarely posing problems in evaporation of glass components during melting. Further, taking into account an evaporation amount of the glass components during melting, it may be necessary to previously change formulation of raw material components. Further, sufficient attention may have to be paid on incidental facilities compared to general glass melting facilities so that the evaporated glass components are not carelessly deaerated outside the glass manufacture facilities. As described above, adopting this method to the fining of the molten glass forcibly and simultaneously requires responses to various problems involved in the method. Therefore, it is not easy for glass manufacturers to adopt this method because

the adoption unfavorably increases limiting conditions.

[0011]

Further, Patent document 6 discloses only the use of helium for the fining of specific borosilicate glass, but proposes nothing about glass materials which can be effectively fining with helium. Therefore, no attempt had been made on developing the method disclosed in Patent document and on applying the method to other glass products with high industrial utility value such as oxide glass.

[0012]

As described above, the conventional methods are hardly satisfying an important object of glass manufacture to manufacture a homogeneous glass product without bubbles. Thus, it becomes to be important for responding to a lot of demands to present glass products that can solve this problem and to supply them in the market.

[0013]

[Means for solving problem]

The inventors of the present invention have found out that it is possible to present a new multicomponent oxide glass that can be melted homogeneously and fundamentally solved the problem involved in the fining during melting, by adjusting the formulation of a polyvalent element and the amount of helium dissolved in glass. Thus, the inventors here present the means for solving the problem.

[0014]

That is, the glass composition of the present invention,

manufactured by melting glass raw materials, is characterized by that the glass composition contains 10 ppm or more of at least one type of a polyvalent element, minimum valence cations of the polyvalent element in a ratio of a minimum valence cation content to a total polyvalent element content of 5 to 98% in mass ratio, and 0.01 to 2 $\mu\text{l/g}$ (0°C , 1 atm) of helium.

[0015]

Here, the phrase of containing 10 ppm or more of at least one type of a polyvalent element means that one or more type of polyvalent elements having two or more types of valences are contained in the glass composition, and a total content of the polyvalent element is 10 ppm or more. A polyvalent element content of less than 10 ppm is not preferable for attaining an effect of the present invention to deaerate bubbles in the glass. Further, generation of the bubbles in the molten glass may greatly vary depending on various external and uncertain melting conditions such as temperature and a flow rate of the molten glass. Therefore, a polyvalent element content is preferably 20 ppm or more for achieving more stable bubble-deaeration property, considering variation in bubble generation. Further, if the glass composition contains 3 or more types of polyvalent elements each of 10 ppm or more, the content of at least one polyvalent element is necessary 50 ppm or more, for achieving high performance of deaerating bubbles from the molten glass. Further, if a glass manufacture rate is $100\text{ cm}^3/\text{minutes}$ or

more, the content of at least one polyvalent element is preferably 100 ppm or more, for surely achieving the performance of deaerating bubbles. Further, if the glass product is used for applications with particularly demanding technical standards on bubble quality in the molten glass, the content of at least one polyvalent element is preferably 200 ppm or more.

[0016]

Further, the phrase of minimum valence cations of the polyvalent element in a ratio of a minimum valence cation content to a total polyvalent element content of 5 to 98% in mass ratio means that with respect to one type of polyvalent element, the content of minimum valence cation of cations of the polyvalent element is within 5 to 98% in mass ratio to the total polyvalent element content.

[0017]

If the ratio of the minimum valence cation content is 5% or more, a function of fining minute air bubbles existing in the molten glass is significant, allowing easy fining of air bubbles of even 1 mm or smaller. If the ratio of the minimum valence cation content is less than 5%, a sufficient function cannot be observed. The ratio of the minimum valence cation content is preferably 10% or more for a sufficiently stable fining function. Further, the ratio of the minimum valence cation content is preferably 15% or more for achieving a sufficiently stable fining effect, preferably 20% or more for achieving a more stable clarification effect, if the glass

composition contains 3 or more types of polyvalent elements. On the other hand, if the ratio of the minimum valence cation content is too large, an amount of gas such as oxygen gas generated accompanying the fining becomes too large. Thus, even if clarification of minute bubbles existing in the molten glass is attained, numerous new bubbles generate and the fining itself becomes difficult. From those views, the ratio of the minimum valence cation content in the glass composition must be 98% or less. That is, if the ratio of the minimum valence cation content exceeds 98%, problem arises in that bubbles remain in the glass products after molding. Further, for glass products required to melt at 1,300°C or more, the ratio of the minimum valence cation content is preferably 95% or less, preferably 90% or less for more assuredly achieving a stable grade of the glass products.

[0018]

Further, the glass composition contains 0.01 to 2 $\mu\text{l/g}$ (0°C, 1 atm) of helium in the present invention. Incorporating a prescribed amount of the helium, which is an inert gas component, as a component for bringing a fining effect of molten glass of multicomponent oxide, in the glass composition allows complete removal or significant reduction of the air bubbles in the molten glass by deaerating the air bubbles from the molten glass, thereby providing a high clarification effect for the multicomponent oxide glass composition.

[0019]

The helium is not involved in network forming of a glass structure, however, the polyvalent element is coexistent in the glass composition, and a ratio of the minimum valence cation content to a total polyvalent element is higher by a predetermined value compared to a case where a glass composition is melted in an oxygen-containing atmosphere, so that a high fining effect is obtained. The helium content providing such an effect must be 0.01 $\mu\text{l/g}$ or more in the glass composition. If the helium content is less than 0.01 $\mu\text{l/g}$, a sufficient fining effect cannot be exhibited. Further, if the helium content is 0.07 $\mu\text{l/g}$ or more, a sure fining effect can be obtained. In addition, to achieve a fining effect even under such a severe condition in that a glass composition contains a large amount of component which is able to turn into a gas, the helium content is preferable 0.11 $\mu\text{l/g}$ or more to provide a molten glass with a sufficient fining effect, thus the deaeration effect of bubbles in the molten glass can be increased.

[0020] On the other hand, if the helium content in the glass composition exceeds 2 $\mu\text{l/g}$, re-foaming called reboiling may likely be observed undesirably through re-heating treatment or the like of the glass composition. A preferable upper limit of the helium content is 1.4 $\mu\text{l/g}$ for inhibiting reboiling, though varying depending on the glass composition, heating conditions, or the like. The preferable upper limit of the helium content shifts to a lower value for a glass composition, in which a clearer except helium

coexists, to as low as 0.9 $\mu\text{l/g}$ because reboiling tends to occur more easily.

[0021]

The inventors of the present invention speculate as follows on how, specifically, a fining effect can be provided when a prescribed amount of the polyvalent element and the helium coexist in the glass composition.

[0022]

The helium is often called an inert gas, a noble gas, or the like, has a stable closed shell structure, and is a monoatomic molecule. Further, the helium is the lightest element among the noble gas elements, and is also structurally very small having an atomic radius of 1.95 angstroms. An attracting force from Van der Waals force of the helium is very small, and thus, the helium does not solidify and is a liquid even at absolute zero at atmospheric pressure. The helium exists as captured in holes of a glass network structure constructed by other components in the glass composition manufactured through high-temperature melting and cooled.

[0023]

On the other hand, the elements constituting the molten glass are generally in a network state having a weak bonding force. The higher the temperature, the more vigorously each element position changes irregularly, accompanied by stretching vibration, rotation vibration, and angular vibration at relatively high speed. As

described above, the helium hardly bonds with various elements constituting the molten glass and has a size enabling passing through gaps of a vibrating network as pathways. Thus, the helium is capable of easily diffusing even to bubbles existing as defects in the molten glass, without being affected by the surrounding elements.

[0024]

When the polyvalent element is dissolved in such molten glass and helium is in existence, the polyvalent element in the molten glass is in existence in a state where the polyvalent element has multiple valences and multiple types of cations each having a different valence exist in a specific ratio. However, coexistence with the helium in the molten glass shifts equilibrium among existence ratio of the multiple types of polyvalent element cations to a direction of increasing the amount of low valence cations. As a result, the amount of the cations having low valences increases in the molten glass while an excess gas component such as oxygen generates along with the equilibrium shift. Then, the generated gas component such as oxygen diffuses with the dissolved helium even to minute air bubbles existing in the molten glass. Thus, diameters of the minute bubbles are expanded to significantly increase a floating rate of the minute air bubbles in the molten glass. As a result, the bubbles in the molten glass are deaerated out of the glass, and thus, the fining takes place.

[0025]

Thus, when the existence ratio of the multiple types of polyvalent element cations is within a predetermined range and a predetermined amount of helium is contained in the molten glass, in other words, when the resolved ratio of the cations and the resolved amount of helium are within predetermined ranges, gaseous components which turn into gas in the glass composition are expedited to be deaerated from the molten glass, thereby, after cooling the molten glass, a homogeneous body of the glass composition can be obtained.

[0026]

The multicomponent oxide glass composition refers to a glass containing two or more types of oxides and the total amount of the two or more types of oxides is 50% or more in mass ratio. More specifically, a glass composition having a single composition with several components mixed as impurities does not fall under the multicomponent oxide glass composition of the present invention. For example, the multicomponent oxide glass composition of the present invention does not apply to a glass composition having close to 99% in mass% of a single component such as silica and 0.09 mass% or less, two decimal places, of the several components respectively.

[0027]

Further, the glass composition of the present invention contains, in addition to the components in claim 1, at least one component of fluorine (F), chlorine (Cl), and sulfur trioxide (SO₃), in a mass ratio of 1 ppm or more, or a OH in a mass ratio of 10

ppm or more.

[0028]

Here, the phrase in which the glass composition of the present invention contains at least one component of fluorine (F), chlorine (Cl), and sulfur trioxide (SO₃), in a mass ratio of 1 ppm or more, or a OH in a mass ratio of 10 ppm or more, means that at least one component of fluorine (F), chlorine (Cl), and sulfur trioxide (SO₃) existing in the glass composition in a mass ratio of 1 ppm or more, or OH group existing in a mass ratio of 10 ppm or more.

[0029]

Various components which may be gasified exist in the glass composition, and among them, a particularly clear effect of the present invention may be observed with F, Cl, SO₃, or the OH group. F, Cl, or SO₃ existing in a mass ratio of 1 ppm or more can enhance an effect of fining the molten glass. The OH group must exist in a mass ratio of 10 ppm or more for exhibiting the same effect as with F, Cl, and SO₃. Enhancement of the fining effect through existence of those components is presumed to result from actions of F, Cl, SO₃, or the OH group during air bubble generation in the molten glass, to suppress generation of numerous bubbles of minute diameters and to generate bubbles with as large diameters as possible.

[0030]

Here, F has a function of promoting the fining by reducing viscosity of the molten glass, but is preferably incorporated in

a mass ratio of 20 ppm or more for more assuredly achieving the fining function. Further, a high-viscosity glass composition melted at 1,400°C or more preferably contains 50 ppm or more of F. On the other hand, since the amount of F added is preferably kept as low as possible from environmental concerns, the amount of F used should be limited even when achieving the present invention. Thus, it is necessary sufficient attention or consideration to employment of F taking account of a application thereof. If F can be replaced with another component, this component should not be employed. Further, an upper limit of the amount of F added should not exceed 0.5% in mass percent in all respects even when no environmental influences are concerned.

[0031]

Further, single use of Cl has been considered to provide a fining effect of the molten glass similar to F, but the effect of the present invention extremely exceeds the fining effect provided using Cl independently. Addition of Cl in a mass ratio of 1 ppm or more provides homogeneous glass through assured fining even for glass considered to be hardly homogenized. Such a hardly-homogenized glass contains preferably 10 ppm or more in mass ratio of Cl added for achieving a higher clarification function, preferably 30 ppm or more thereof added for achieving highly stable clarification that is not affected by operational or furnace conditions or the like. Further, if a large amount of the helium

cannot be added for various circumstances, the added helium must be definitely used for the fining. In such a case, 100 ppm or more of Cl is preferably incorporated. The hardly-homogenized glass such as no-alkali glass contains preferably 200 ppm or more of Cl added, possibly 300 ppm or more thereof added for achieving a more stable effect.

[0032]

Further, SO_3 is added in the glass by employing a sulfate as a raw material and have been used for providing a fining effect from solubility of SO_3 in the molten glass being large at low temperature and being small at high temperature. However, the effect of the present invention extremely exceeds the fining effect provided using SO_3 independently, and such an effect can be provided by adding 1 ppm or more of SO_3 in mass ratio. A glass composition with low reactivity at high temperatures contains preferably 20 ppm or more of SO_3 added, preferably 50 ppm or more thereof added for providing a more stable effect. A glass composition requiring high temperature of $1,400^\circ\text{C}$ or more for melting thereof preferably contains 300 ppm or more of SO_3 added.

[0033]

An effect of the OH group similar to F or the like have attracted attention to reduce high-temperature viscosity of the glass, allowing easy floating of the bubbles in the molten glass. The OH group is known to possess a clarification function similar to F.

However, the effect of the present invention extremely exceeds the clarification effect of the OH group used independently, and such an effect may be provided by adding 10 ppm or more of the OH group in mass ratio. A glass composition having high high-temperature viscosity and requiring 1,200°C or more for melting thereof contains preferably 40 ppm or more of the OH group added, preferably 60 ppm or more thereof for more stably achieving the effect. Further, 100 ppm or more of the OH group may be added for cases where a sufficient addition amount of the helium cannot be ensured.

[0034]

Further, in addition to the contents described in claim 1 or claim 2, the glass composition of the present invention is characterized in that, the ratio of the content of the minimum valence cations of the polyvalent element to the polyvalent element content is higher by 0.1 to 40% compared to that of a glass composition manufactured by melting in an oxygen-containing atmosphere.

[0035]

Here, the phrase in which the ratio of the content of the minimum valence cations of the polyvalent element to the polyvalent element content is higher by 0.1 to 40% compared to that of a glass composition manufactured by melting in an oxygen-containing atmosphere, means that the ratio of the content of the minimum valence cations existing in the molten glass to the total amount of the polyvalent element is higher by 0.1 to 40% compared to that of a glass composition

manufactured by melting in an atmosphere containing 1% or more oxygen. The polyvalent element in the molten glass is in existence in a state where the polyvalent element has two or more types of cations each having a different valence. Of these cations, the existence ratio of the minimum valence cations to the total amount of the polyvalent element is higher by 0.1 to 40% compared to that of a glass composition manufactured by melting in an atmosphere containing 1% or more oxygen.

[0036]

If the oxygen content is less than 1%, the ability of deaerating bubbles from the molten glass is decreased. If the oxygen content is 3% or more, this ability is less subjected to other operating conditions of melting furnace and the like to be more stable. Further, it is more preferable if the oxygen content is 5% or more, since bubbles can be deaerated in less time. Furthermore, if the oxygen content is 1% or more, an efficient fining effect can be achieved in even as a glass composition turning into a molten glass with high viscosity in which bubbles of 1mm and the like are hard to be deaerated. Such a ratio is particularly preferable for a glass composition requiring melting at 1,400°C or more.

[0037]

In addition, when the ratio of the content of the minimum valence cations of the polyvalent element to the polyvalent element content is 40% or less, compared to that of a glass composition manufactured

by melting in an oxygen-containing atmosphere, it is preferable to achieve a bubble deaeration effect from the molten glass of the present invention. If the value is more than 40%, it is not preferable since the bubble deaeration effect is low. Further, the value is preferably 30% or less for the molten glass having a viscosity of 10^3 dPa·s at a temperatures of 1,000°C or more, preferably 20% or less for achieving a more stable bubble deaeration function.

[0038]

The above oxygen-containing atmosphere means an atmosphere wherein at least 1% in volume or more oxygen is contained, which including, as a matter of course, normal atmosphere or a high oxygen concentration atmosphere. In any case, oxygen exists in the atmosphere.

[0039]

Further, in addition to the contents described in any one of claims 1 to 3, the glass composition of the present invention is characterized in that, 1 ppm or more of the polyvalent element is existent in the glass composition in the state of cations having one or more valences.

[0040]

Here, the phrase in which 1 ppm or more of the polyvalent element is existent in the glass composition in the state of cations having one or more valences means that the polyvalent element in the present invention is able to exist in the oxide glass composition in the

state of having one or more types of positive atomic valences. That is, the polyvalent element being able to constitute an oxide and having positive atomic valences is changed in valence of the element in the molten glass of high temperature to cause oxidation-reduction reaction. A gas such as oxygen result from the reaction diffuses into minute bubbles in the molten glass together with helium to notably accelerate dilatation of bubbles in the molten glass. As a result, deaeration of bubbles from the molten glass is prompted so that a fining effect is achieved.

[0041]

The reason why 1 ppm or more of the polyvalent element existent in the glass composition is necessary to exist in the state of having positive atomic valence is that if it is less than 1 ppm, the gas such as oxygen sufficient to be able to dilate bubbles is not generated. In such the condition, the oxidation-reduction reaction that brings a sufficient fining effect is not induced. Therefore, it is necessary for the present invention that 1 ppm or more of the polyvalent element having positive atomic valence is existent in the glass composition.

[0042]

To achieve more stable deaeration function of bubbles and to achieve high fining effect even to a high viscosity molten glass, it is more preferable that 3 ppm or more of the polyvalent element existent in the glass composition has positive atomic valence. In addition, when the existence amount of the polyvalent element is

100 ppm or more, it is important that the polyvalent element having minimum valence has one or more types positive valences, that is, the element is existent in the glass composition at least 5 ppm or more as cations.

[0043]

Further, the polyvalent element is preferably an element having a first ionization energy of 6 to 10 eV. An effect of promoting bubble deaerate from the molten glass tends to be high apparently, particularly when the first ionization energy of the polyvalent element, the energy required for the polyvalent element to deaerate an electron to become a cation, is within the above range. A reason for such has not been revealed, but the inventors of the present invention presume that when the energy required for transition to a different electronic state falls within a prescribed range, an equilibrium constant of oxidation-reduction equilibrium regarding the polyvalent element in the molten glass changes through diffusion of the helium into the molten glass. The oxidation-reduction equilibrium changes relatively, and thus, gas such as oxygen is easily deaerated.

[0044]

Further, in addition to the contents described in any one of claims 1 to 4, the glass composition of the present invention is characterized in that, the polyvalent element is any one of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Y, Zr, Mo, Rh, Ag, Cd, Sn,

Sb, Te, Ti, Pt, Au, and Bi.

[0045]

Here, the phrase in which the polyvalent element is any one of vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), germanium (Ge), arsenic (As), selenium (Se), yttrium (Y), zirconium (Zr), molybdenum (Mo), rhodium (Rh), silver (Ag), cadmium (Cd), tin (Sn), antimony (Sb), tellurium (Te), titanium (Ti), platinum (Pt), gold (Au), and bismuth (Bi), means that these element are especially existent in the glass composition and the existence ratio of the minimum cations is within the predetermined rage.

[0046]

The glass composition contains at lease one of these polyvalent elements of 10 ppm or more, wherein the ratio of the content of the minimum valence cations of the polyvalent element to the polyvalent element content is higher by 0.1 to 20% compared to that of a glass composition manufactured by melting in an oxygen-containing atmosphere, and contains the predetermined amount of helium, thereby, the glass composition has a high performance which can deaerate minute bubbles from the molten glass thereof to become a homogeneous glass.

[0047]

The glass composition of the present invention, which is a multicomponent oxide glass composition, may contain at least two

types of elements which may become cations as elements constituting the glass in addition to the polyvalent element and further contains oxygen as an element which may become an anion.

[0048]

Further, in addition to the contents described in any one of claims 1 to 5, the glass composition of the present invention is characterized in that the divalent cation content of Sn to the total Sn content is 20 to 50%.

[0049]

Here, the phrase in which the divalent cation content of Sn to the total Sn content is 20 to 50%, means that the existence amount of the divalent cation Sn^{2+} in the molten glass, which is the minimum valence cation of Sn, to the total amount of Sn^{2+} and the tetravalent cation Sn^{4+} is within the range of 20 to 50%. Sn is often used in manufacture of sheet glass, in refractive index adjustment of optical glass, or the like. If the ratio is less than 20%, the fining ability from the molten glass of the glass composition is inferior. Thus, the ratio is necessary to be 20% or more, preferably, 23% or more to achieve a more stable function. Reversely, if the ratio is more than 50%, the number of generated bubbles tends to be too great, and also the bubbles often become minute bubbles with small diameter. Therefore, the upper limit of the ratio is 50%. The upper limit of the ratio is preferably 45% to accelerate deaeration of bubbles from the molten glass more surely. As for a non-alkalis glass, the

content of the divalent cation of Sn is preferably more than 26% and not more than 40%.

[0050]

Further, in addition to the contents described in any one of claims 1 to 6, the glass composition of the present invention is characterized in that a ratio of the trivalent cation of Sb to the total Sb content is 70% or more.

[0051]

Here, the phrase in which a ratio of the trivalent cation of Sb to the total Sb content is 70% or more, means that the existence amount of the trivalent cation Sb^{3+} to the total amount of Sb^{3+} and the pentavalent cation Sb^{5+} is 70% or more. Sb is often used as a fining agent for the molten glass. The lower limit in ratio of the trivalent cation is necessary to be 70%. If the ratio is less than the lower limit of 70%, there is often a problem in which prompt deaeration of minute bubbles from the molten glass is not made. To achieve a fining of minute bubbles from the molten glass more surely, the ratio of the trivalent cation is preferably 80% or more. As for a non-alkalis glass, the content of the trivalent cation of Sb is preferably 91% or more, more preferably 92% or more.

[0052]

Further, in addition to the contents described in any one of claims 1 to 7, the glass composition of the present invention is characterized in that a ratio of the trivalent cation of As to the

total As content is 60% or more.

[0053]

Here, the phrase in which a ratio of the trivalent cation of As to the total As content is 60% or more, means that the existence amount of the trivalent cation As^{3+} to the total amount of As^{3+} and the pentavalent cation As^{5+} is 60% or more. As is used as a fining agent for the molten glass similar to Sb. It becomes to be possible to give a high fining ability to the glass, since the existence amount of the trivalent cation of As to the total amount of As in the glass composition is 60% or more. If the content ratio of the trivalent cation of As is less than 60%, it is not able to deaerate bubbles in the molten glass sufficiently to make the glass homogeneous, especially as for a glass material which is necessary to melt at a temperature of 1300°C or more. To achieve this ability more surely, it is preferable that the content ratio of the trivalent cation of As is 70% or more.

[0054]

Further, in addition to the contents described in any one of claims 1 to 8, the glass composition of the present invention is characterized in that a ratio of the divalent cation of Fe to the total Fe content is 30% or more.

[0055]

Here, the phrase in which a ratio of the divalent cation of Fe to the total Fe content is 30% or more, means that the existence

amount of the divalent cation Fe^{2+} to the total amount of Fe^{2+} and the trivalent cation Fe^{3+} is 30% or more. Fe is added to the glass for purposes such as glass coloring and enhancing infrared absorption ability or is mixed into the glass by employing a silica or alumina raw material or the like of not high-purity. By controlling valence of Fe component in glass, more effective fining can be given to many glass materials. To achieve an effective fining, it is necessary that the ratio of the divalent cation of Fe to the total amount of the divalent cation of and the trivalent cation of Fe is 30% or more. If the ratio of the divalent cation of Fe in the glass is less than 30%, it is difficult to deaerate bubbles with diameter of 1mm or less in the molten glass of the composition sufficiently efficiently. To achieve this effect more surely, it is preferable that the content ratio of the divalent cation of Fe is 40% or more.

[0056]

Further, the glass composition of the present invention can appropriately contain: colorants such as other transition metal compounds, tellurium compounds, selenium compounds, rare earths, and sulfides exhibiting color with various colored ions, additives causing colloid coloring such as a CdS-CdSe solid solution, and radiation coloring additives such as Ce; and additives of scarce metal elements for adjusting transmittance or refractive index. Further, in contrast, elements such as U, Th, Pb, Ra, and K may be finely controlled as appropriate to a ppm order or a ppb order.

to allow melting of the glass so that the molten glass contains a minimal amount of the elements, to deal with demands from applications employing the glass composition.

[0057]

Further, the glass composition of the present invention can respond to various manufacture conditions according to applications including: ion exchange treatment for imparting desired properties such as strength property and optical property; provision of various thin films to a glass surface; implantation of specific ion species to the glass surface; glass surface treatment with chemicals for improving surface property of the glass or the like; solidification of radioactive substances or toxic substances; rapid-quenching vitrification and molding using liquid nitrogen, liquid helium, or the like; glass manufacture by ultra-high temperature melting using solar energy or the like; special glass manufacture using a phenomenon of crystallization or the like under ultra-high pressure conditions; and inclusion of specific additives for imparting other special electromagnetic properties to the glass.

[0058]

Further, an example of the raw materials which can be used for manufacturing the glass composition of the present invention includes materials containing: a single substance, a mixture, or a compound of inorganic substances such as oxides, carbonates, phosphates, chlorides, and various glass as a main component; and

a single substance, a mixture, or a compound of organic additives, metal additives, or the like in addition to the above various inorganic substances as an additive. Classification of the glass based on source of glass materials such as natural products, synthetic products, or purified products does not matter. Further, highly purified industrial products, with impurities in a ppm order or a ppb order removed through various methods, can be employed as raw materials of the glass composition of the present invention. Further, general raw materials for glass manufacture, manufactured and purified in mining and chemical industry and used, may also be used as raw materials of the glass composition of the present invention.

[0059]

Further, melting of the glass raw materials generally involves: collectively maintaining the glass raw materials in a heat-resistant container of ceramics, platinum, or the like as while supplying energy from a heat source such as electricity or gas; and then melting the materials while preventing the multiple raw materials from separating during high-temperature heating. However, methods which may be employed as appropriate include: applying external force such as current pressure and electromagnetic force; and floating the molten glass above the liquid metal.

[0060]

[Function]

As described above, the glass composition of the present invention, manufactured by melting glass raw materials, is characterized in that the glass composition contains 10 ppm or more of at least one type of a polyvalent element, minimum valence cations of the polyvalent element in a ratio of a minimum valence cation content to a total polyvalent element content of 5 to 98% in mass ratio, and 0.01 to 2 $\mu\text{l/g}$ (0°C, 1 atm) of helium, allowing deaeration of minute bubbles in the molten glass from the molten glass by rapidly dilating diameters of the bubbles.

[0061]

The glass composition of the present invention further containing at least one of 1 ppm or more in mass ratio of F, Cl, and SO_3 , or 10 ppm or more in mass ratio of OH, making it possible to dilate minute bubbles without making the number of bubbles in the molten glass significantly increased.

[0062]

Further, the glass composition of the present invention, wherein the ratio of the minimum valence cation content to the total polyvalent element content is higher by 0.1 to 40% in mass ratio compared to the ratio of a glass composition manufactured by melting in an oxygen-containing atmosphere, making it possible to control a fining effect of the molten glass precisely, by controlling the content ratio of cations.

[0063]

The glass composition of the invention, wherein 1 ppm or more of the polyvalent element is existent in the glass composition in the state of cations having one or more valence, making it possible to achieve homogenization of even a high viscous molten glass which is difficult to fined, by controlling valences of the polyvalent element existent in the glass to contribute to dilatation of bubbles due to generated gas such as oxygen.

[0064]

Further, the glass composition of the present invention, wherein the polyvalent element is any one of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Y, Zr, Mo, Rh, Ag, Cd, Sn, Sb, Te, Ti, Pt, Au, and Bi, contributes to glass coloring and to an improvement in chemical durability, in addition to the clarification effect. Further, the selected polyvalent element can impart various functions of high levels to the glass composition, in addition to homogeneity.

[0065]

In addition, when the divalent cation content of Sn to the total Sn content is 20 to 50%, or the trivalent cation content of Sb to the total Sb content is 70% or more, or the trivalent cation content of As to the total As content is 60% or more, or the divalent cation content of Fe to the total Fe content is 30% or more, it is possible to manufacture a homogeneous glass product with no bubbles, with satisfying a wide range of functions required to glasses.

[0066]

[Embodiment of the invention]

Hereinafter, the glass composition of the present invention will be described in detail by way of examples.

[0067]

[Example 1] The inventors of the present invention have conducted a research following a procedure described below to confirm fining performance of a glass composition of the present invention. First, Table 1 shows the researched glass compositions. In Table 1, reference symbol A represents no-alkali glass with poor melting property, and reference symbol B represents glass with excellent melting property, containing relatively high amounts of alkali metal elements. Reagent grade, high purity glass raw materials were selected to yield the glass compositions shown in Table 1, and preliminary analysis confirmed that the amounts of impurities or the like can be sufficiently grasped as well. The raw materials were weighed and then subjected to mixing for 1 hour using a rotary raw material mixer, to thereby prepare a raw material batch subjected to sufficient mixing. Then, the raw material batch was charged into a platinum-rhodium crucible. The crucible was placed in an indirect electric resistance furnace maintained at a prescribed temperature, and then maintained at 1,550°C for 2 hours, to thereby cause a vitrification reaction. The batch was subjected to 4 more hours of melting while adjusting a helium content in the glass by introducing

helium, gas adjusted to 50 to 99.9% concentration with nitrogen, into the furnace through a gas supply pipe.

[0068]

Subsequently, molten glass was cooled to room temperature inside the furnace slowly cooled, and investigations were conducted by gathering samples required for determination of the number of bubbles in the glass obtained, for analysis of helium (He) gas in the glass, and for analysis of the polyvalent elements. Determination of the number of bubbles involved both visual observation and observation using a microscope of 20 power magnification. Further, helium gas was analyzed using a quadrupole mass spectrometer (QMA125, manufactured by Balzers AG) installing a secondary electron multiplier (SEM) for improving measurement sensitivity. Gas analysis using the quadrupole mass spectrometer involved: placing a required amount of glass sample to be measured in a platinum dish, keeping the platinum dish in a sample chamber to vacuum of 10^{-5} Pa (that is, 10^{-8} Torr); and introducing the gas heated and deaerated into the quadrupole mass spectrometer having a measuring sensitivity of 0.001 $\mu\text{l/g}$.

[0069]

Further, valences of the polyvalent elements in the glass were analyzed using necessary analyzers or the like after the obtained glass was decomposed with an acid or dissolved in an alkali. Sn and Sn^{2+} were analyzed through the following mode, for example. Part

of a glass block cooled was used for chemical analysis to determine the total amount of existing Sn and Sn^{2+} . The total amount of existing Sn and Sn^{2+} was determined through instrumental analysis and redox titration after the glass was decomposed in an acidic solution. Further, an amount of Sn^{2+} was indirectly determined by titrating the amount of Fe^{2+} , formed from reduction by Sn^{2+} in the decomposed solution, with a cerium sulfate solution. To be specific, the total amount of Sn was determined by preparing a sample solution through heat decomposition of glass powder with sulfuric acid and hydrofluoric acid and subsequent dissolution of the decomposed glass powder in hydrochloric acid and by using an ICP-AES device. Sn^{2+} was heat decomposed for 10 minutes (in water bath) in an inert gas environment by first adding 2 ml of a 0.1% Fe^{3+} solution to the glass powder and then adding the sulfuric acid and the hydrofluoric acid thereto. During the heat decomposition, Fe^{3+} was reduced by Sn^{2+} to form Fe^{2+} . Subsequently, boric acid was added to the resultant solution to neutralize the excess hydrofluoric acid, and then introduction of the inert gas was stopped. Then, 1 ml of a 0.015 M OsO_4 solution was added to the resultant solution as a catalyst of the present invention, and 1.0 ml of an o-phenanthroline indicator was added. Sn^{2+} was analyzed and an amount thereof was determined through indirect titration involving titrating with a 1/200 N cerium sulfate solution until color of the solution changed from orange to pale blue.

[0070]

[Table 1]

Glass name Components (mass%)	A	B
SiO ₂	59.0	61.5
Al ₂ O ₃	16.3	2.1
B ₂ O ₃	9.0	-
CaO	5.3	-
SrO	6.1	9.0
BaO	3.1	9.7
ZnO	1.0	0.5
Na ₂ O	-	7.5
K ₂ O	-	7.5
TiO ₂	-	0.6
ZrO ₂	0.2	1.6

[0071]

Table 2 shows the obtained results. Glass types in Table 2 correspond to glass names in Table 1. As shown in Table 2, glass were prepared by adding 1.0% in mass ratio of As, Sb, or Sn as an oxide of the polyvalent element and adjusting a ratio of the minimum valence cation content to the polyvalent element content. In samples 1 to 9, the number of bubbles in the glass after melting was 1 to 136 bubbles per 10 g of glass.

[0072]

[Table 2]

Sample	1	2	3	4	5	6	7	8	9
Glass type	A	A	A	A	A	A	A	A	A
Type of polyvalent element oxide	As ₂ O ₃	As ₂ O ₃	As ₂ O ₃	Sb ₂ O ₃	Sb ₂ O ₃	Sb ₂ O ₃	SnO ₂	SnO ₂	SnO ₂
Amount of	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

polyvalent element oxide added (mass%)									
(Amount of minimum valence cations)/(amount of polyvalent elements) x 100	75	77	80	91	92	96	27	28	29
He content (μl/g-glass : 0°C, 1 atm)	0.0 1	0.0 2	0.0 5	0.01	0.0 4	0.05	0.0 2	0.0 4	0.0 7
Number of bubbles (bubbles/10 g-glass)	15	9	1	136	120	70	31	20	1

[0073]

[Comparative Example 1] Melting was conducted following a similar procedure as in Example 1 and using the same device as in Example 1, except that the melting was conducted in air for 4 hours instead of in helium for 4 hours in the final step as in Example 1 (step of melting while introducing helium). Table 3 shows the results.

[0074]

[Table 3]

Sample	10	11	12
Glass type	A	A	A
Type of polyvalent element oxide	As ₂ O ₃	Sb ₂ O ₃	SnO ₂
Amount of polyvalent element oxide added (mass%)	1.0	1.0	1.0
(Amount of minimum valence cations)/(amount of	72	90	26

polyvalent elements) x 100			
He content ($\mu\text{l/g-glass}$: 0°C , 1 atm)	<0.01	<0.01	<0.01
Number of bubbles (bubbles/10 g-glass)	46	182	115

[0075]

As (arsenic), which is the same polyvalent element as in the samples 1, 2, and 3 in Table 2, was used for the sample 10 in Table 3. Sb (antimony), which is the same polyvalent element as in the samples 4, 5, and 6 in Table 2, was used for the sample 11 in Table 3. Sn (tin), which is the same polyvalent element as in the samples 7, 8, and 9 in Table 2, was used for the sample 12 in Table 3. However, comparing the samples of Example 1 and Comparative Example 1 by the types of polyvalent elements added confirmed that the number of bubbles in the glass in Example 1 was significantly reduced compared to the glass in Comparative Example 1. Further, analysis of the helium content in the glass in Comparative Example 1 (samples 10 to 12) resulted in a low value of less than $0.01 \mu\text{l/g}$, probably mixed from air or the like.

[0076]

Further, As^{3+} content ratios (ratios of As^{3+} contents to total As contents) of the samples 1, 2, and 3 in Table 2 were respectively 75%, 77%, and 80% in mass ratio, As^{3+} being the minimum valence cation of As. Those values were higher by 3%, 5%, and 8% compared to the As^{3+} content ratio of the sample 10 in Table 3 of 72%. Similarly,

Sb³⁺ content ratios (ratios of Sb³⁺ contents to total Sb contents) of the samples 4, 5, and 6 in Table 2 were respectively 91%, 92%, and 96% in mass ratio, Sb³⁺ being the minimum valence cation of Sb. Those values were higher by 1%, 2%, and 6% compared to the Sb³⁺ content ratio of the sample 11 in Table 3 of 90%. Further, Sn²⁺ content ratios (ratios of Sn²⁺ contents to total Sn contents) of the samples 7, 8, and 9 in Table 2 were respectively 27%, 28%, and 29% in mass ratio, Sn²⁺ being the minimum valence cation of Sn. Those values were higher by 1%, 2%, and 3% compared to the Sn²⁺ content ratio of the sample 12 in Table 3 of 26%.

[0077]

[Example 2] Melting was conducted following a similar procedure as in Example 1, using the same device as in Example 1 and using glass raw materials containing sulfates, chlorides, and hydroxides so that amounts of SO₃, Cl, and OH added could be changed. Table 4 shows the results.

[0078]

[Table 4]

Sample	13	14	15	16		17		18	
Glass type	B	B	B	A		A		A	
Type of component added	SO ₃	SO ₃	SO ₃	Cl	OH	Cl	OH	Cl	OH
Content of component added in glass (mass%)	0.1 4	0.1 2	0.0 5	0.1 6	0.0 14	0.1 5	0.0 12	0.1 3	0.00 6
He content (μl/g-glass: 0°C, 1 atm)	0.0 1	0.0 3	0.0 7	0.01		0.04		0.06	

Number of bubbles (bubbles/10 g-glass)	4	2	1	47	28	16
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[0079]

The samples 13, 14, and 15 were glass containing sulfates, as raw materials, added to glass B shown in Table 1, providing homogeneous glass with a very little number of bubbles in the glass. Further, the samples 16, 17, and 18 were glass containing chlorides and hydroxides, as raw materials, added to glass A shown in Table 1, providing glass with 16 to 47 bubbles per 10 g of glass, which is a sufficiently small number of bubbles in the glass.

[0080]

[Comparative Example 2] Melting was conducted following a similar procedure as in Example 2 and using the same device as in Example 2, except that the melting was conducted in air for 4 hours instead of in helium for 4 hours in the final step as in Example 2 (step of melting while introducing helium). Table 5 shows the results.

[0081]

[Table 5]

Sample	19	20	
Glass type	B	A	
Type of component added	SO ₃	Cl	OH
Content of component added (mass%) in glass	0.20	0.17	0.019

He content ($\mu\text{l/g-glass: } 0^\circ\text{C, } 1$ atm)	<0.01	<0.01
Number of bubbles (bubbles/10 g-glass)	10	145

[0082]

The sample 19 in Table 5 was glass containing SO_3 added to glass B, similar to the samples 13, 14, and 15 in Table 4, providing glass with a larger number of bubbles compared to the samples 13, 14, and 15 because helium was not introduced. Further, the sample 20 of Table 5 was glass containing Cl or OH added to glass A, similar to the samples 16, 17, and 18 in Table 4, providing glass with a significantly larger number of bubbles, 145 bubbles per 10 g of glass, compared to the samples 16, 17, and 18 because helium was not introduced.

[0083]

[Example 3] Based on the above results, the inventors of the present invention have attempted to introduce the helium gas into an actual continuous melting furnace manufacturing a glass product shown in Table 6, to thereby improve the bubble quality. The glass product shown in Table 6 is used for image display devices such as liquid crystal displays.

[0084]

[Table 6]

(mass%)

Glass name	SiO ₂	Al ₂ O ₃	MgO	Li ₂ O	Na ₂ O	K ₂ O	P ₂ O ₅	ZrO ₂	TiO ₂	As ₂ O ₃
C	65.8	22.3	0.6	4.1	0.6	0.4	1.4	2.3	2.0	0.5

[0085]

The melting furnace used for manufacturing the above glass product is a tank melting furnace provided with a first melting chamber, a second melting chamber, and a fining chamber. The furnace is provided with two heat sources of gas firing and electrodes. The furnace has a maximum melting temperature of 1,600°C and requires 48 hours of residence time for the molten glass. The helium was introduced from hearth of the first melting chamber through a heat-resistant gas introducing pipe into the molten glass at 30 l/minutes. The fining effect of and dissolved components in the glass manufactured as above were analyzed. As a result, 0.08 µl/g of helium was dissolved in the glass, and a ratio of the minimum valence cation (As³⁺) content to the total As content was 76% in mass ratio. In addition, the glass had 1 air bubble/kg glass, and enhanced homogeneity and improved efficiency percentage by 1.2% compared to conventional products.

[Document] ABSTRACT OF THE DISCLOSURE

[Abstract]

[Problem] To present a glass composition which makes it possible to conduct fining surely in melting of a multicomponent oxide glass to obtain a homogeneous glass product.

[Means for solving problem] A glass composition of the present invention is a glass composition of a multicomponent oxide glass manufactured by melting glass raw materials, containing 10 ppm or more of at least one type of a polyvalent element, minimum valence cations of the polyvalent element in a ratio of a minimum valence cation content to a total polyvalent element content of 5 to 98% in mass ratio, and 0.01 to 2 $\mu\text{l/g}$ (0°C, 1 atm) of helium, and further containing at least one of 1 ppm or more in mass ratio of F, Cl, and SO_3 , or 10 ppm or more in mass ratio of OH.